the solution separated, dried over calcium chloride, and distilled. The yield of benzophenone was 4.6 g.; the substance melted at 48° after recrystallization from ether.

Summary

1. Triphenyl-chloromethane is converted by ethers in the presence of aluminum chloride into triphenylmethane.

2. The reaction has been utilized to develop a convenient method of preparation of triphenylmethane from carbon tetrachloride, benzene, aluminum chloride and ether.

3. When the alkyl ethers or esters derived from triphenyl carbinol are heated an excellent yield of triphenylmethane is obtained.

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THE STRENGTH OF TRIMETHYLAMINE OXIDE AND TRIMETHYL ALKOXYL AMMONIUM HYDROXIDES AS BASES. THE STRUCTURE OF AMMONIUM COMPOUNDS

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The real basicity of trimethylamine oxide hydrate, $(CH_3)_3NO.2H_2O$, and the basicity of alkoxyl derivatives formed from it by the reaction, $(CH_3)_3NO \xrightarrow{RI} [(CH_3)_3NOR]\ I \xrightarrow{AgOH} [(CH_3)_3NOR]\ OH$, have long been in question. Dunstan and Goulding[1] state that the properties of the aqueous solutions of the free alkoxyl ammonium bases show them to be "strongly basic substances." Meisenheimer[2] describes the amine oxides as "very weak bases, much weaker than ammonia" and the alkoxyl ammonium salts as "colorless, strongly acid reacting substances . . . ." Hantsch and Graf[3] deduced from the conductivity of the salts of the amine oxide that only very slight hydrolysis takes place in solution. Noyes and Hibben[4] found qualitatively that the conductivities of solutions of the free bases were much less than the conductivities of the respective salts.

Much speculation has been based on the assumption of weak basicity in these compounds. Michael[5] has represented the structure of the

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[1] Dunstan and Goulding, *J. Chem. Soc.*, **75**, 792 (1899).

[2] Meisenheimer, *Ann.*, **397**, 284 (1910).

[3] Hantsch and Graf, *Ber.*, **38**, 2156 (1905).

[4] Noyes and Hibben, THIS JOURNAL, **45**, 355 (1923).

[5] Michael, *ibid.*, **42**, 1238 (1920). A complete discussion of previous work, with references, is given in this paper. No attempt is to be made here to fix completely the structure of the ammonium ion portion of these salts. Michael assumed that the mechanism by which aldehydes are formed on decomposition involved hydrolysis, and since an alkoxyl group must hydrolyze to an alcohol, the structure should not be represented as containing an alkoxyl group. However, chlorine attached to nitrogen

methoxy derivative as the hydro-iodide of a complex base, $(CH_3)_3\text{-}\overline{\text{NOC}}\text{H}_2\text{.HI}$ on the grounds, in part, that Meisenheimer's formula for the salt, $[(CH_3)_3N{-}O{-}CH_3]I$, does not suggest an acid reaction in solution or explain the production of formaldehyde on heating with alkali: $[(CH_3)_3NOCH_3]I + NaOH \longrightarrow (CH_3)_3N + H_2CO + NaI + H_2O$. Noyes and Hibben[4] cite the weak basicity as evidence that *five* groups are attached to nitrogen in the case of the free ammonium hydroxides.

This paper deals with an attempt to obtain some quantitative data on the strength of these bases and the conclusions which may be drawn from the results.

Experimental Results

Purification of Salts.—The halogen acid salts of trimethylamine oxide are readily purified by crystallization from hot alcohol or from hot water and drying in a vacuum desiccator. The possibility of adsorption of traces of free acid in the crystals cannot be eliminated, but since the degree of hydrolysis is large it is believed that no serious error arises from this source. Consistent results on successive purification were used as an indication of purity.

The purification of the alkoxyl derivatives is more difficult, and although consistent results were obtainable upon recrystallization, using the method of Meisenheimer,[6] and the analyses and physical properties corresponded with those obtained by him, it was impossible to be certain that traces of the highly hydrolyzed salts of the oxide itself were not present. Measurements on these preparations are given (Table II). Subsequently it was found possible to prepare a more satisfactory product, as described below (Table III), but no method of purification eliminated the acid reaction of these salts in water.

The Degree of Hydrolysis of the Salts.—Since the free alkoxyl bases decompose more or less readily into tertiary amine and aldehyde, it was at first thought advisable to measure the degree of hydrolysis of the salts. The determination of the acidity of standard aqueous solutions of the salts by means of the hydrogen electrode was attempted. A known volume of 0.5 *N* acid was added to the salt solution, and the mixture titrated as usual with 0.5 *N* alkali. Reproducible curves could be ob-

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hydrolyzes to hypochlorous acid, so that if hydrolysis is part of the mechanism, an anomalous hydrolysis of an alkoxyl group in this case is not surprising. Similar results on the hydrolysis of nitrite and nitrate esters are common. On the other hand, none of the facts, strength of base, method of preparation, or known reactions, really distinguishes between the formulas $[R_3NOCH_2R]I$ and $[R_3NC(OH)HR]I$. Since we have no valid reason at present for discarding the former and accepted structure, it will be assumed here that the alkyl radicals remain intact during and after the addition of the alkyl halide to the amine oxide, and that a corresponding alkoxyl group is therefore formed.

[6] Meisenheimer, *Ann.*, **397**, 273 (1913).

tained, but even after alkali equivalent to both acid and salt had been added, the voltage was only about 0.58 volt, and the solution apparently acid. At that point it smelled strongly of amine and was alkaline to phenolphthalein. In view of this, it was not considered safe to use the hydrogen electrode even in solutions of the pure salts, and resort was had to a colorimetric method.

To 50 cc. of the salt solution in a colorimeter tube were added two drops of indicator, and the color was matched with that of liquid in another tube containing the same amount of indicator, conductivity water and 0.005 *N* hydrochloric acid to make a total volume of 50 cc. Table I gives the results of the experiments on the degree of hydrolysis of the salts of the amine oxide.

TABLE I

HYDROLYSIS OF SALTS OF TRIMETHYLAMINE OXIDE

Temperature, 20°

Salt soln. 50 cc.	Concn. *M*	Cc. of 0.500 *N* HCl in 50 cc.	H + concn.	$KB \times 10^{10}$	Indicator
$(CH_3)_3NOHCl$	0.0845	22.00	2.2×10^{-3}	1.9	Methyl violet
		20.05	2.0×10^{-3}		
$(CH_3)_3NOHI$	.0850	21.20	2.1×10^{-3}	1.9	
$(CH_3)_3NOHBr$	.1760	30.50	3.05×10^{-3}	1.9	
$(CH_3)_3Br$	.0880	19.84	1.98×10^{-3}	2.2	
$(CH_3)_3NOHCl$	.0041	2.70	26×10^{-5}	5.6	Methyl orange
		2.56			
$(CH_3)_3NOHCl$	.00205	2.02	20×10^{-5}	4.7	
$(CH_3)_3NOHI$	.00452	2.68	27×10^{-5}	5.8	
		2.73			
$(CH_3)_3NOHI$	.00226	2.07	21×10^{-5}	4.6	
		2.10			
				Av. 3.8	

This result is qualitatively verified by the fact that the amine oxide is too weak a base to affect phenolphthalein.

Table II gives the acidity of solutions of different preparations of alkoxyl derivatives. These salts had the characteristics of those described by previous investigators. The dissociation constants for the bases are not calculated, since later results indicate that the acidity must be due to impurities. The results, however, are given for comparison with earlier work.

Three other preparations, one of the methoxy iodide, one of ethoxy iodide and one of ethoxy bromide, gave similar results. If the values in Table II are to be considered valid the dissociation constant of these alkoxyl bases would be about 1% that of ammonia, or 10^{-7}. The salt of such a base, on titration with sodium hydroxide, using phenolphthalein, would use up almost one equivalent of base, that is, the weak base would be barely strong enough to affect phenolphthalein and would be almost completely liberated by the stronger base before the end-point was reached. However, when the alkoxyl salts were subjected to this test, the end-point to phenolphthalein was always reached before 5% of an equivalent of base had been added. The conclusion drawn was that the acid reaction of the salt was due to impurity present in small amount, probably some of the amine oxide salt.

Table II

Acidity of Aqueous Solutions of Alkoxyl Ammonium Salts

Temperature, 20°. Indicator, methyl orange

Salt soln. 50 cc.	Concn. *M*	Cc. of 0.005 *N* HCl in 50 cc.	H^+ concn.
$(CH_3)_3NOCH_3I$	0.0814	0.52	
		.48	4.8×10^{-5}
		.45	
$(CH_3)_3NOCH_3I$	.0407	.35	
		.38	3.5×10^{-5}
		.33	
$(CH_3)_3NOC_2H_5I$	.0084	1.58	15.9×10^{-5}
		1.60	
$(CH_3)_3NOC_2H_5I$	.0042	2.32	23.0×10^{-5}
		2.30	
$(CH_3)_3NOC_4H_9O$	.0974	4.0	4.0×10^{-5}
$(CH_3)_3NOC_2H_5I$	.0957	0.59	5.9×10^{-5}

In attempting to prepare very pure samples of the ethoxyammonium iodide, it was found possible to raise the decomposition point from 122–124°, given by Meisenheimer, to 135–136°.

Preparation of Pure Trimethylethoxyammonium Iodide.—Dehydrated amine oxide was prepared from the hydrate by essentially the method used by Noyes and Hibben. The hydrate (15 g.) was placed in a bomb tube, connected through a calcium chloride tower to a pump and evacuated to 5–10 mm. pressure. The tube was then immersed in an oil-bath and the temperature held at 100–110° until boiling ceased. At this point about half the water was removed. The temperature was then held at 115–120° until boiling had again ceased and the melt had solidified to needle-like crystals, after which the temperature was raised during 30–60 minutes to 180°. The portion of the bomb outside the bath was heated with a free flame to remove water from small amounts of sublimed hydrate. Very little of the dehydrated oxide was sublimed. The tube and content (10 g.) were then cooled in a freezing mixture of salt and ice, and about 31 g. (1.5 moles) of cooled ethyl iodide was added. The amine oxide dissolved slowly in the ethyl iodide, and when solution was nearly complete the mixture was poured into a small flask, the tube washed out with about 10 cc. of absolute alcohol and the clear solution left to stand overnight in a small ice-bath. In the course of an hour after mixing the reagents the solution deposited a solid mass of crystals. After this time it was found safe to bring the mixture to room temperature. The heating specified by previous investigators was omitted. Various methods were used in working up the mush of crystals. A satisfactory procedure is to filter by suction, wash the crystals with about 10 cc. of absolute alcohol and dry in a desiccator over phosphorus pentoxide. To the mother liquor and washings are added 2cc. portions of ether until further addition gives but a slight precipitation, and analysis of the solution indicates not more than a few tenths of a gram content of iodide ion. For recrystallization the two portions may be combined, and dissolved in methyl alcohol (1 cc. per g.), in ethyl alcohol (2 cc. per g.), in butyl alcohol (3 cc. per g.) or in glacial acetic acid (2 cc. per g.). When the alcohols are used the solution is filtered while warm (60°), allowed to cool in an ice-bath while protected from the air to prevent deposition of water, filtered, washed with mixtures of alcohol and ether and finally with ether. The filtrate is treated with ether as described above. The glacial acetic acid solution may be warmed if necessary to hasten solution. The filtration in this case is usually very slow if the crude product is very impure. The filtered solution is fractionally precipitated with ether and the crystals are washed thoroughly with butyl alcohol and ether before drying. The acetic acid solvent was found necessary in obtaining a pure product from the crude when only a slight excess of ethyl iodide, large amounts (20–50 cc.) of alcohol, and heating were used in the preparation.

The pure product crystallizes as fine leaflets, analyzing within experimental error for the true iodine content (54.97%). The decomposition point, contrary to Meisenheimer's statement, is perhaps the best criterion of purity. The temperature of decomposition varies somewhat with the rate of heating and samples have been obtained which decomposed from 135–136°. Most samples of the fairly pure product decomposed within 1° between 133° and 135°. The total yield, including all fractions containing between 54.5% and 55.0% of iodine and decomposing above 130° was 19.5 g., or 65% of that calculated.

The preparation of the methoxy derivatives was carried out in the same manner. Extreme care must be taken to prevent development of too great heat when the methyl iodide is added to the amine oxide, as the reaction is very vigorous. A 53% yield was obtained of a product analyzing correctly and decomposing at about 165°. Considerable tetramethylammonium iodide was formed and also low iodine products which will be described elsewhere.

The ethoxy derivative is not decomposed when heated with glacial acetic acid for an hour at 100°. Heated with alkali it gives a strong odor of acetaldehyde. These pure products were still found to give a slight acid reaction in water, but the following means was adopted to show that they were the salts of a strong base.

Conductivities of Trimethyalkoxyl Ammonium Hydroxides.—The conductivities of a given salt solution and of a given sodium hydroxide solution were determined. The conductivities of mixtures of the two solutions were then compared with the conductivities of mixtures of each with sufficient conductivity water to make the same dilution. If no association of ions occurred the conductivity of a mixture composed of 5 cc. of each solution would be approximately the sum of the conductivities of each solution diluted separately with an equal volume of water. The same pipet was used in measuring the different solutions. The cell constant was not determined, as the same cell was used throughout. The results are expressed in the last column of Table III as conductivities in reciprocal ohms of this cell when filled as shown.

The results show that there is no association of ions on mixing equal molal quantities of the salt and sodium hydroxide amounting to more than 2% of the ions originally present and that, therefore, the trimethyl alkoxyl ammonium hydroxides are very strong bases.

No change in the conductivities was observed when the alkaline mixture stood in the thermostat for an hour. Over the week-end the conductivity of a solution containing 1 mole of salt and 0.5 mole of sodium hydroxide decreased about 25%, due to decomposition into the weaker base trimethylamine.

TABLE III

CONDUCTIVITY OF ALKOXYL AMINE SALT SOLUTIONS, OF SODIUM HYDROXIDE AND OF MIXTURES

Temperature 25°

Total volume Cc.	Volume NaOH (0.02 *M*) Cc.	Volume salt (0.04 *M*) Cc.	Volume H_2O Cc.	$C \times 10^2$
SODIUM HYDROXIDE SOLUTION				
10	5	...	5	0.724
15	10	...	5	.961
$(CH_3)_3NOC_2H_5I$				
10	..	5	5	0.631
15	..	5	10	.430
MIXTURE OF $(CH_3)_3NOC_2H_5I$ AND NaOH				
10	5	5	..	1.328
Calc. (0.724 + 0.631)				1.355
15	10	5	..	1.363
Calc. (0.961 + 0.430)				1.391
$(CH_3)_3NOCH_3I$				
10	..	5	5	0.680
15	..	5	10	.464
MIXTURE OF $(CH_3)_3NOCH_3I$ AND NaOH				
10	5	5	..	1.371
Calc. (0.724 + 0.680)				1.404
15	10	5	..	1.390
Calc. (0.961 + 0.464)				1.425

Ionization of the Salts.—That the alkoxyl ammonium iodides in solution are highly ionized is shown by their conductivity. In addition, it was found that solutions of these iodides precipitated lead iodide from solutions of lead nitrate in the same molal concentrations as did sodium iodide. There is no evidence that the salts are weak electrolytes.

Vapor Pressure of Trimethylamine Oxide Hydrate.—A slow stream of air containing water vapor of about 12 mm. partial pressure, was passed over the anhydrous amine oxide at 25°. The issuing air contained water vapor of 2.5–3.0 mm. pressure. When about 1 mole of water had been absorbed per mole of amine oxide a slight decrease in the partial vapor pressure of the water was observed. As nothing was determined regarding the composition of the solid phase, nothing can be said except that the pressure of water vapor over the hydrate is not greater at 25° than 2.5 mm.

Discussion of Results

Trimethyl alkoxyl ammonium salts are salts of very strong bases, whereas the trimethylhydroxyl ammonium salt is a salt of a very weak base. It has long been recognized that a quaternary ammonium hydroxide is a very strong base when all four substituting groups in the ammonium radical are alkyl groups. When one of these alkyl groups is substituted by hydroxyl there is a marked decrease in basicity. The ion $(CH_3)_3NOH^+$, therefore, must react almost completely with hydroxyl ion to form an un-ionized substance while the ions R_4N^+ and R_3NOR^+ do not react appreciably with hydroxyl ion.

In the case of a tertiary amine salt reacting with a base, the reaction is usually represented by the equilibria, $R_3N\overset{+}{H} + \overset{-}{OH} \rightleftharpoons R_3N\text{-}HOH \rightleftharpoons R_3N + H_2O$, and the weak basicity of the amine is ascribed either to the formation of an un-ionized hydrate or to a low degree of hydration of the amine, or both. In most cases the hydrates are at least very unstable, and where hydration is formally complete, as in the true quaternary derivatives, we have strong bases. In the case of trimethylamine oxide hydrate, however, we have shown that the stability of the hydrate is too great to assume that the weak basicity is due to lack of hydration,[7] and therefore another factor must be considered. Noyes and Hibben[4] believed that this represented one case in which there was real association of the hydroxyl ion with the ammonium ion, and represented the weak base as a nitrogen atom with five groups attached: $R_3N(OH)_2$.

The Lewis theory of atomic structure, however, suggests in the case of nitrogen a maximum of four points of attachment. Lewis[8] predicted the strong basicity of these alkoxyl ammonium bases on the assumption that not more than four groups could be attached to the nitrogen atom, and that unless the fifth or negative group could associate in some other

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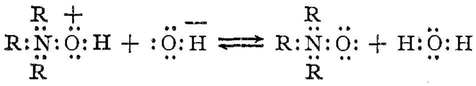
[7] It is assumed that there is only one kind of hydration. If it be assumed that the stability of a solid hydrate is due to its crystalline arrangement, that stability may then not be used to prove that the substance in solution must be hydrated. Moreover, the hydration of the type which produces hydroxyl ion when an amine is dissolved in water may be fundamentally different from "water of crystallization" or "water of hydration."

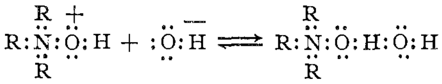
[8] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, **1923**, p. 111. At the time of the publication of this monograph only the results given in Table II above were available. These at the time seemed in agreement with the results of Noyes and Hibben, that the conductivity of the trimethylethoxyammonium hydroxide was much smaller than that of the corresponding salt. Our later results (Table III) and further work on the preparation of the pure salts led to complete verification of Professor Lewis's original ideas as to the relation between structure and properties of ammonium compounds. We cannot explain the results of Noyes and Hibben, unless the free base decomposed under their treatment or formed insoluble silver complexes to such an extent as to reduce greatly the amount of the base in solution, thereby reducing the conductivity.

position in the molecule such a quaternary compound must be a strong base. In the case of the trimethylhydroxyammonium ion, however, the hydrogen ion may either dissociate,



$$\mathrm{R}:\overset{\mathrm{R}\;+}{\underset{\mathrm{R}}{\ddot{\underset{..}{\mathrm{N}}}}}:\ddot{\underset{..}{\mathrm{O}}}:\mathrm{H} + :\overset{..\;-}{\underset{..}{\mathrm{O}}}:\mathrm{H} \rightleftharpoons \mathrm{R}:\overset{\mathrm{R}}{\underset{\mathrm{R}}{\ddot{\underset{..}{\mathrm{N}}}}}:\ddot{\underset{..}{\mathrm{O}}}: + \mathrm{H}:\ddot{\underset{..}{\mathrm{O}}}:\mathrm{H}$$

or attract an hydroxyl ion,



$$\mathrm{R}:\overset{\mathrm{R}\;+}{\underset{\mathrm{R}}{\ddot{\underset{..}{\mathrm{N}}}}}:\ddot{\underset{..}{\mathrm{O}}}:\mathrm{H} + :\overset{..\;-}{\underset{..}{\mathrm{O}}}:\mathrm{H} \rightleftharpoons \mathrm{R}:\overset{\mathrm{R}}{\underset{\mathrm{R}}{\ddot{\underset{..}{\mathrm{N}}}}}:\ddot{\underset{..}{\mathrm{O}}}:\mathrm{H}:\ddot{\underset{..}{\mathrm{O}}}:\mathrm{H}$$

the hydrogen acting as a link between the two ions in the latter case and forming an un-ionized hydrate. Neither of these reactions can take place with the alkoxyl derivatives. This explanation of the reaction is more satisfactory than the assumption that we have in the amine oxide hydrate a case of five groups or radicals attached to the nitrogen atom itself. In fact the amine oxide attaches not one but two molecules of water as a solid, and perhaps more in solution, and this ability to form complexes still exists to a small extent apparently in the salts, and even in the alkoxyl derivatives. Evidence of this will be presented in another paper.

Summary

The dissociation constant of trimethylamine oxide hydrate as a base has been determined and found to be about 4×10^{-10}. The trimethyl alkoxyl ammonium hydroxides derived from it are strong bases of the quaternary type. There is no evidence in this field that a nitrogen atom may unite by primary valence forces with more than four groups or radicals.

Pure trimethylethoxyammonium iodide decomposes sharply at 135–136°.

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